CHAPTER 5

The Effect of Sewage Sludge and Biosolids on Uptake of Trace Elements and Reactions in Soil

INTRODUCTION

The reactions of trace elements and plant micronutrients in soil and their uptake and accumulation by plants affect the availability to animals and humans. The state of trace elements in soils generally falls into the following categories:

- Soluble
- Exchangeable
- Insoluble inorganic precipitates
- Chelated/complexed on organic matter or its fractions
- Adsorbed on inorganic colloids
- As minerals

The uptake of trace elements and plant micronutrients depends on the soluble equilibrium and exchangeability of an element and, therefore, its concentration in the soil solution. Adsorption mechanisms are important in determining the availability of the metal to plants. In addition to adsorption by soil organic matter, metal adsorption by reactive soil surfaces is important. Corey et al. (1981) indicated that adsorption on mineral surfaces is probably the dominant process controlling metal solution activities. Activity is generally considered as effective concentration.

When metals are added through the application of biosolids, solution metal activities would be controlled by adsorption to biosolids and soil mineral surfaces, as long as the amount of metal added did not exceed the capacity of specific surface adsorption sites in the soil. Some have suggested that the metal chemistry of a particular biosolid may be important in the availability of the metal to plants.

Heavy metals can also revert with time to chemical forms less available to plants (Epstein and Chaney, 1978). Sposito et al. (1983) found that Zn from biosolids reverted to the less available carbonate form over time. However, metal reversion in

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soil is small and/or slow and can be reversed by soil acidity (Logan and Chaney, 1983). The form of the heavy metal in soil affects its solubility and, therefore, the potential for movement through the soil and uptake by plants. This section discusses the regulated heavy metals and other trace elements in soils and plants. Throughout this chapter, the term "trace elements" will be used except when a specific literature citation uses the term "heavy metals."

The soil factors that affect trace element uptake are:

- Soil pH — Soil pH is the most important factor controlling metal solubility. The concentration in the soil solution is governed by an equilibrium between adsorbed and dissolved forms. With the exception of Mo and Se, all the essential trace elements are more soluble at low pH. The solubility of metal carbonates, phosphates and sulfides is increased at low pH (Lindsey, 1979). Heavy metals are more available to plants below pH 6.5 (Chaney, 1973; CAST, 1980). The solubility of most heavy metals or trace elements increases as the acidity of the soil increases. There is an approximately 100-fold decrease in activity (effective concentration) of Zn and Cu for each unit increase in soil pH. At low pH, heavy metals are more soluble (in the soil solution) and mobile. This increases their potential uptake by plants and potential for movement through the soil profile. Anderson and Christensen (1988) showed the pH is more important than any other single property in controlling Zn mobility.
- Organic matter — Organic matter can bind and complex certain heavy metals so that they are less available to plants. Organic matter has a high cation exchange capacity (CEC) compared to the mineral fraction of soils. This factor is important in binding such heavy metals as Cu, Zn, Ni and Cd. Organic matter can also chelate heavy metals, reducing their availability to plants. This property might be more important than the simple cation-exchange role of the organic matter.
- Elemental interactions — Certain elements can interact with some heavy metals to decrease their availability to plants. The availability of heavy metals to plants and their mobility through the soil is dependent on interactions with other elements. The hydrous oxides of Fe and Mn can control the availability of heavy metals by sorption and desorption (Jenne, 1968; Quirk and Posner, 1975). Phosphorus combines with metal ions to form soluble or insoluble complexes (Epstein and Chaney, 1978). Barrow (1987) showed that orthophoshates could either increase or decrease Zn retention in soil depending on pH. McBride (1985) reported that there was a decrease in sorption of Cu in soils when orthophosphates were present. Cadmium retention in the soil is influenced by Fe content.
- Soil Cation Exchange Capacity (CEC) — This factor is important in the binding of heavy metals and other cations (Chaney, 1973; CAST, 1976). This includes all the regulated trace elements except those that occur as anions in the soil solution. Soils with low CEC such as sands have a much lower binding power as compared to clays with a high CEC. Organic matter has a high CEC and contributes to the total CEC of soils and the binding power to heavy metals. Recognition of the importance of CEC in the availability of metals to plants resulted in early recommendations and regulations relating heavy metal additions to land based on CEC (USEPA, 1980). Three CEC categories of soil were established: <5, 5–15, >15 meq/100 g soil. However, at a later date it was difficult to establish a direct

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relationship between CEC and metal uptake. Consequently, in the 40 CFR 503 regulations, this relationship was omitted.

- Soil water, soil temperature and soil aeration — These factors affect heavy metal uptake by plants. Soil water affects the amount of trace elements in the soil solution. As the soil dries, the heavy metals in solution become more concentrated and can precipitate or be adsorbed on soil colloids and become unavailable to plants. Soil water can affect the chemical state of the metal.

Epstein (1971) showed that temperature increased the concentration of Mn, P and Ca in potato tops and roots. Soil aeration affects the oxidation and reduction conditions in the soil. Under submerged conditions, reduction occurs with a decrease in Eh and an increase in pH (Lindsay, 1979). Under reduced conditions, probably only Fe and Mn are more apt to be available to plants.

PLANT UPTAKE OF HEAVY METALS

Plant uptake of trace elements affects the concentration of the metal in plant tissues and can affect human and animal nutrition or phytotoxicity. The uptake of trace elements by plants involves several mechanisms. For uptake by plant roots, the trace element must move from the soil to the plant root. The principal mechanisms are convection and diffusion (Chaney, 1975). As water moves through the soil, it solubilizes plant nutrients and trace elements, including heavy metals. Plants absorb water and through convective flow and metals enter the root system. At the root surface elemental movement is governed by the rate of diffusion. One of the more important phenomena that affect trace element movement to roots is chelation. Organic matter is the most important chelating agent. Once the trace element enters the root system, at least two phases involve movement and accumulation in upper plant tissues (Chaney, 1975). The first phase involves movement to and release into the xylem sap and the second involves movement in the xylem sap to plant tissues. Uptake of water and ions occurs in two separate pathways (Kochian, 1991). A detailed discussion of micronutrient reactions in soil and uptake by plants can be found in *Micronutients in Agriculture* (Mortvedt et al., 1991).

Chaney (1980) introduced the concept of "soil-plant-barrier." Chaney (1983) states a soil-plant-barrier protects the food chain from toxicity of a trace element when one or more of the following processes limits maximum levels of that element in edible plant tissues to levels safe for animals:

- Insolubility of the element in soil prevents uptake
- Immobility of an element in fibrous roots prevents translocation to edible plant tissues
- Phytotoxicity of the element occurs at concentrations where the element, in edible plant tissues, is below a level that is injurious to animals.

Chaney (1994) states that the soil-plant-barrier concept showed that soil and plant chemistry prevents risk to animals from nearly all biosolids-applied trace elements mixed in the soil.

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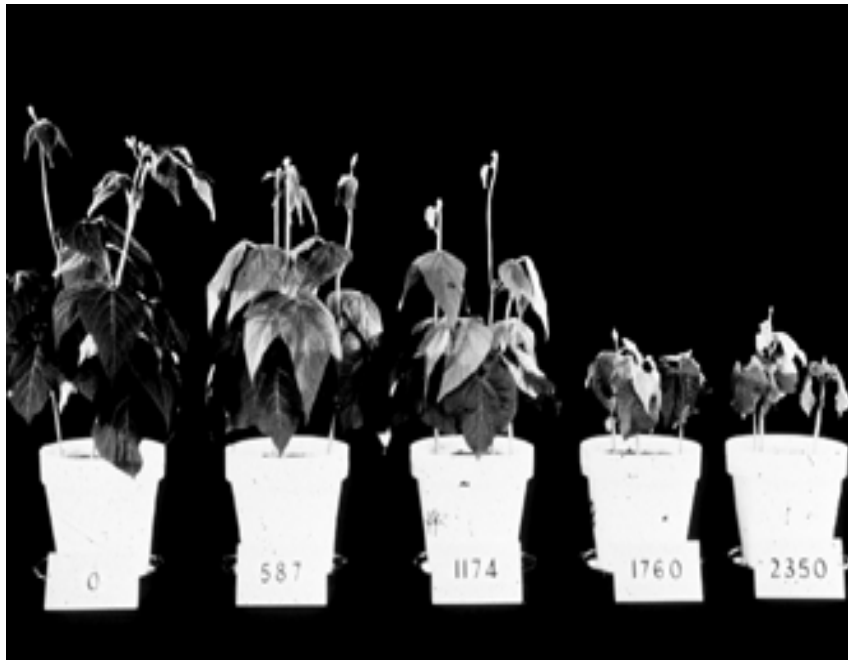

Figure 5.1 Effect of nickel toxicity on snap beans. Dosage of nickel ranges from 0 to 235.0 mg/kg. (Courtesy of Dr. R. Chaney, USDA.)

Phytotoxicity can be manifested by excessive trace element adsorption and result in injury or death to plants. In biosolids, the elements most likely to be phytotoxic are Cu, Ni and Zn. Cu and Ni toxicity retards growth and can inhibit Fe translocation, resulting in Fe deficiency and chlorosis. The effect of nickel on phytotoxicity of snap beans is shown in Figure 5.1. Zn toxicity can also result in retarded growth and symptoms similar to Fe deficiency. Phytotoxicity is affected by soil pH, crop species and cultivars, biosolids' metal concentration and other soil and climatic factors. Table 5.1 shows the relative sensitivity of crops to biosolid-applied trace elements.

The uptake of trace elements by plants is a function of the concentration of the element, soil characteristics, climate, plant species, or cultivars (Chang et al., 1982, 1987; Giordano et al., 1979; Hinsely et al., 1982). Chaudri et al. (2001) indicated that uptake of Cd by wheat was strongly influenced by soil pore water. Bingham et al. (1975) showed that Cd content of plants varies according to plant species and plant tissue as shown in Figure 5.2. Cereals and legumes accumulated less Cd in the shoot than leafy vegetables.

Kim et al. (1988) evaluated the relative concentrations of Cd and Zn in tissues of 12 selected food plants. They found that the relative concentration of these metals in several sludge-treated soils was significantly different. Figure 5.3 shows the cadmium content of harvested plant parts as related to soil cadmium. Higher Cd in the soil resulted in a higher Cd content in plant organs. The leaves contained the highest Cd content, followed by the root or tuber, with the least in the fruit, seed,

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Table 5.1 Relative Sensitivity of Crops to Biosolids-Applied Trace Elements*

Very sensitive[1]	Sensitive[2]	Tolerant[3]	Very tolerant[4]
Chard	Mustard	Cauliflower	Corn
Lettuce	Kale	Cucumber	Sudan grass
Red beet	Spinach	Zucchini squash	Smooth bromegrass
Carrot	Broccoli	Flat pea	Red fescue
Turnip	Radish	Oat	
Peanut	Tomato	Orchard grass	
Lidino clover	Zigzag, Red Kura and crimson clover	Japanese bromegrass	
Alsike clover	Alfalfa	Switchgrass	
Crown vetch	Korean lespedeza	Redtop	
Alfalfa	Sericea lespedeza	Buffalo grass	
White sweet clover	Blue lupine	Tall fescue	
Yellow sweet clover	Bird's-foot trefoil	Red fescue	
Weeping love grass	Hairy vetch	Kentucky bluegrass	
Lehman love grass	Soybean		
Deertongue	Marigold		
	Snapbean		
	Timothy		
	Colonial bent grass		
	Perennial ryegrass		
	Creeping bent grass		

* Sassafras sandy loam amended with highly stabilized and leached digested biosolids containing 5300 mg Zn, 2400 mg Cu, 320 mg Ni, 390 mg Mn, 23 mg Cd/kg dry biosolids.
[1] Injured at 10% of a high metal biosolid at pH 6.5 and pH 5.5.
[2] Injured at 10% of a high metal biosolid at pH 5.5 but not at pH 6.5.
[3] Injured at 25% high metal biosolid at pH 5.5, but not at pH 6.5; and not at 10% biosolid at pH 5.5 or 6.5.
[4] Not injured even at 25% biosolid, pH 5.5.

Source: Courtesy of Dr. R. Chaney, USDA.

or flower. Table 5.2 shows the relative concentrations of Cd in various plants with respect to the Cd content of the soil.

Jing and Logan (1992) showed that the chemistry of the biosolids and its trace element concentration had some effect on plant uptake. They found that Cd concentrations in Sudax [*Sorghum bicolor* (L.) Moench] taken up from 17 anaerobically digested biosolids were highly correlated with total and resin-extractable biosolid Cd, even though the total Cd application to the soil was constant.

Table 5.3 shows the concentration of cadmium, zinc, copper and nickel in edible portions of vegetables grown on sewage sludge from 1977 through 1979 (Corey et al., 1987). The data illustrate several important aspects of metal uptake.

- Leafy vegetables such as Swiss chard and spinach accumulated more Cd and Zn than non-leafy vegetables.
- The uptake of Cu and Ni was not much different in all the vegetables. Thus, crop uptake varies from one metal to another.
- Root crops such as beets and carrots did not accumulate more metals than above-ground edible organs such as tomatoes and green beans.

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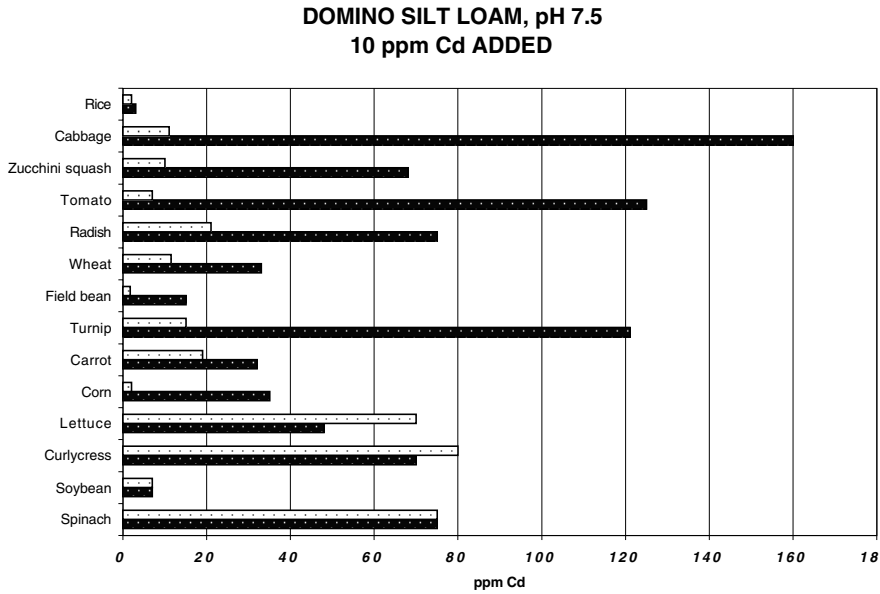
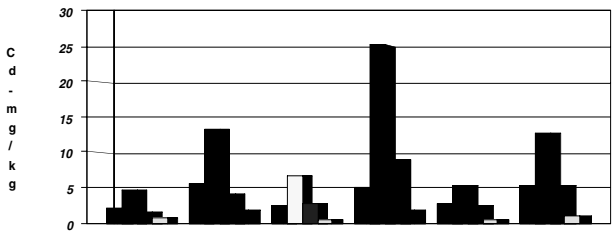


Figure 5.2 Cadmium content in edible and nonedible portions of plants. (Adapted from Bingham et al., 1975.)



	Las Virgines I	Las Virgines II	Greenfield I	Greenfield II	Domino I	Domino II
Soil	2.1	5.6	2.4	5.1	2.8	5.3
Leaves	4.69	13.23	6.71	25.08	5.43	12.7
Root/Tuber	1.73	4.14	2.73	9.12	2.49	5.4
Fruit/Seed/Flower	0.89	1.94	0.44	2	0.5	1.1

Figure 5.3 Cadmium content of harvested plants as related to soil cadmium. (Adapted from Kim et al., 1988.)

Brown et al. (1996) evaluated the uptake of Cd by a variety of fruits and vegetables grown on long-term biosolids-amended soils. They found that it was possible to establish a useful, quantitative relationship between the concentrations of Cd in lettuce to the other vegetables in the study. They suggested that this relationship could establish a means of assessing possible risk associated with Cd contamination.

Relatively few long-term biosolids field studies took place during the 1970s and 1980s. Page et al. (1987) indicated that several long-term studies on plant uptake of metals from sewage sludge/biosolids revealed some important findings:

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Table 5.2 Relative Concentrations of Cd in Plant Organs for the Low- and High-Cd Las Virgenes Soils, Using Swiss Chard as the Reference Plant

Plant	Las Virgenes I 2.1 mg/kg Cd	Las Virgenes II 5.6 mg/kg Cd
Swiss chard	1.0	1.0
Tomato leaf	2.5	0.2
Tomato fruit	0.2	0.01
Pepper leaf	8.5	3.3
Pepper fruit	1.6	0.7
Leaf lettuce	3.1	2.7
Head lettuce	2.8	3.3
Radish leaf	2.0	2.4
Radish tuber	0.6	0.6
Potato leaf	0.54	0.79
Potato tuber	0.41	0.55
Corn leaf	1.0	0.5
Corn kernel	0.1	0.06
Wheat leaf	0.6	0.2
Wheat grain	0.2	0.1
Broccoli leaf	0.6	0.9
Broccoli flower	0.1	0.4
Carrot leaf	3.0	1.3
Carrot root	1.8	0.9
Beet leaf	1.5	1.4
Beet root	0.5	0.2

Source: Adapted from Kim et al., 1988.

- Plant uptake is a function of plant species, individual trace elements, soil characteristics and sludge/biosolids characteristics.
- Sludge/biosolids is both a source and a sink for trace elements.
- Trace element uptake by plants may obey many different rate response functions: linear, sympatric, no response, or even negative.

Subsequently, many researchers have found that the uptake by various crops was not linear with trace elements or sludge/biosolids' application rate, but rather approached a maximum and then leveled or decreased (Chaney and Ryan, 1992; Logan and Chaney, 1983; Corey et al., 1987). This phenomenon was called the plateau response. For low-metal biosolids, the phytoavailability is controlled by the biosolids' chemistry (Brown et al., 1998).

Beckett et al. (1979) suggested that the organic matter in biosolids is responsible for the binding effect of metals. McBride (1995) contended that as the organic matter decomposed, trace elements will be released into more soluble forms and result in increased uptake from biosolids. He termed this hypothesis as the "time bomb" effect. Chang et al. (1997) indicated that the "sludge time bomb hypothesis" may show a plateau effect during the course of biosolids' application. The issue is what happens when the addition of biosolids organic matter decomposes. Once the biosolids organic matter is lost, will the metals become more available? McBride (1995) stated, "Because soils have a finite capacity to immobilize metal by adsorption or

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Table 5.3 Concentration of Cadmium, Zinc, Copper and Nickel in Edible Portions of Plants Grown on Sludge-Amended Soil

	Amount of Biosolids Applied to Land – tonnes/ha				
Crop	0	60	120	240	300
	Cadmium – mg/kg in edible tissue				
Beets	0.2	1.4	1.6	2.7	2.9
Tomatoes	1.1	1.8	2.4	2.2	3.4
Swiss chard	2.3	8	12.2	16.8	22.1
Carrots	0.7	1.4	1.2	1.9	2.3
Green beans	0.4	0.3	0.4	0.4	0.5
Spinach	6.4	12.6	10.3	14.4	12.1
	Zinc – mg/kg in Edible Tissue				
Beets	34	45	62	93	90
Tomatoes	27	30	30	34	35
Swiss chard	69	129	176	237	302
Carrots	20	22	25	27	32
Green beans	32	33	37	37	37
Spinach	147	249	265	309	311
	Copper – mg/kg in Edible Tissue				
Beets	8.8	10.4	9.8	11.1	12.8
Tomatoes	13.2	16.6	14.5	16.2	16.6
Swiss chard	23.7	20.8	25.4	30.9	29.2
Carrots	5.4	6.0	5.8	5.9	6.5
Green beans	8.6	8.9	9.2	8.2	8.5
Spinach	13.8	14.2	17.3	18.9	19.1
	Nickel – mg/kg in Edible Tissue				
Beets	0.5	0.6	0.9	1.4	1.5
Tomatoes	1.1	1.3	1.4	4.1	2.7
Swiss chard	1.3	1.4	2.5	3.5	4.3
Carrots	1.9	0.7	0.8	1.2	1.0
Green beans	3.3	1.2	2.4	3.6	3.3
Spinach	1.4	1.5	1.7	2.7	2.6

Source: Corey et al., 1987, pp. 25–51, A.L. Page et al. (Eds.), *Land Application of Sludge*, Lewis Publishers, Chelsea MI. With permission.

precipitation reactions, without the protective effect of the sorptive material in the sludge itself, a Langmuir-type relationship would be expected."

The plateau effect implies that biosolids are both a source and a sink for trace elements applied to soil. At low biosolids' application, the soil binds the elements and plant uptake is linear. At very high biosolids' application rates, the biosolid matrix influences the binding of trace elements. The plateau theory, therefore, posits that the concentrations of heavy metals in plant tissue will reach a plateau as biosolids mass loadings are increased and they will remain at a plateau after the termination of biosolids' application. Chang et al. (1997) used a set of experimental data obtained from a 10-year field biosolids' land application to evaluate the hypotheses of the plateau and the time bomb. They indicated that with those set of data, an actual plateau or time bomb was not evident. Biosolids' application had reached 2880

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Mg/ha, which probably represented a worst-case scenario in terms of pollutant loading.

However, there are other factors that affect the binding of trace elements in the soil. Furthermore, the rate of soil organic matter decomposition will be rapid initially when the soluble carbohydrates, fats and some proteins are microbially metabolized. Once these fractions are assimilated by microorganisms, then hemicellulose, cellulose and lignin — that are very significant in metal binding — are slow to decompose.

Complexation of trace elements is with the humified fraction in the soil that decomposes very slowly. The organic fraction in biosolids is generally 50% to 60%. The remainder for the most part is inert. Approximately 40% to 50% of this organic matter is fairly rapidly decomposed. The remainder is very slow to decompose. Therefore, it is highly unlikely that all the organic matter will disappear and make the bound trace elements available for plant uptake.

Several studies have shown that organic matter from sludge and manure additions to soils may still be present in significant quantities in the soil for long periods of time. As much as 50% of organic carbon remained in the soil after 10 years of land application sludge or manure (Johnston, 1975; Johnston and Wedderburn, 1975).

Brown et al. (1998) found that, 16 years following application, there was no significant increase in Cd by lettuce, even though a significant portion of the organic carbon from the biosolids had disappeared. They indicated that the addition of biosolids altered the soil chemistry so that the incremental increase in plant availability of soil Cd in the soil/biosolids mixture was less than that of the soil alone. They further determined that increases in Cd adsorption in biosolids-amended soils appeared to be related to the inorganic complexing ability added to the soil with biosolids.

Sloan et al. (1998) evaluated the recovery of biosolids-applied heavy metals 16 years after application. The results of the study showed that biosolids organic matter decomposes slowly when applied to a well-drained silt loam in a temperate climate. Therefore, the rapid release of biosolids-derived heavy metals is unlikely to occur.

In an earlier paper, Sloan et al. (1997) reported that biosolids-applied Cd existed in chemical forms that were easily extracted from soil and were readily available for uptake by romaine lettuce. The most easily extracted forms of Cd (i.e., exchangeable and specifically adsorbed) accounted for approximately 75% of total Cd in biosolids-amended soil. Biosolids-applied Cr, Cu, Ni, Pb and Zn were in relatively stable soil chemical forms and were not correlated to plant uptake. Concentrations of Cd, Zn, Cu, Ni and Cr in romaine lettuce were positively correlated to total concentrations of the respective metals in soil.

Data by Bidwell and Dowdy (1987) showed that Cd and Zn availability to corn, following termination of land application of sewage sludge, decreased with time. Corn was sampled for 6 years after termination of three annual applications of sewage sludge. Cumulative sludge applications totaled 0, 60, 120 and 180 Mg/ha.

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Table 5.4a Concentration of Cadmium in Corn Stover and Grain for Six Years Following Three Annual Applications of Biosolids Sludge to Soil

Year	Control	Low	Medium	High
		Corn Stover		
1	0.23	3.41	4.96	9.83
2	0.18	1.48	3.22	5.18
3	0.11	0.82	1.72	4.56
4	0.06	1.15	1.78	2.14
5	0.08	1.82	3.35	3.26
6	0.08	0.88	1.26	1.93
		Corn Grain		
1	<0.06	0.10	0.11	0.27
2	<0.04	<0.05	0.07	0.06
3	<0.02	<0.03	0.07	0.15
4	<0.01	<0.03	0.02	0.05
5	<0.02	0.04	0.04	0.06
6	0.02	0.03	0.04	0.06

Source: Adapted from Bidwell and Dowdy, 1987.

Table 5.4b Concentration of Zinc in Corn Stover and Grain for Six Years Following Three Annual Applications of Sewage Sludge to Soil

Year	Control	Low	Medium	High
		Corn Stover		
1	19.9	88.9	101	140
2	31.9	72.8	119	153
3	18.7	66.5	87.3	121
4	30.8	88.0	105	107
5	25.7	112	114	154
6	18.5	66.6	75.8	105
		Corn Grain		
1	25.6	37.0	37.4	44.7
2	32.8	41.0	42.1	50.7
3	27.6	39.3	46.8	72.2
4	35.9	45.2	39.5	43.3
5	36.7	55	55.4	55.3
6	29.6	37.3	38.8	39.4

Source: Adapted from Bidwell and Dowdy, 1987.

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Tables 5.4a and 5.4b show some of their data. The data highlight several points:

- Cadmium and Zn concentrations in corn stover and grain increase with sludge applications where high levels of the metals are applied to the soil.
- There was a decrease in the concentration of Cd and Zn in both the corn stover and grain, with time, following application of sewage sludge.
- The corn grain contained significantly lower concentrations of the metals than the stover. In fact, for most of the treatments and time, there was no difference in Cd concentration in the grain.

Logan (1997) conducted a field study from 1991 to 1995. He found that different trace elements behaved differently following biosolids' application. Cadmium, Cu and Zn concentrations in corn increased significantly with biosolids' application, while Ni and Pb levels were lower than the control. Cadmium, Cu and Zn concentrations in corn exhibited a plateau-type response. Lettuce concentrations increased linearly with biosolids' application for Cd, Cu and Zn in all years; linear regression slopes generally declined and stabilized after the first 2 years.

Table 5.5 Mean Concentration of Trace Metals in Corn Stover and Grain Over Time

Year	Treatment	Zn	Cu	Cd	Pb	Ni	Cr
			Stover Concentration - mg/kg				
1–5	Control	16.1	5.0	0.14	1.9	0.7	1.0
6–10		17.7	6.0	0.10	0.9	0.8	1.4
11–19		18.0	8.4	0.16	0.9	0.7	0.9
1–5	Biosolids	23.0	5.8	0.16	1.6	0.8	1.0
6–10		60.2	7.2	0.18	1.0	1.2	2.8
11–19		46.5	7.0	0.18	0.8	0.6	0.4
			Grain Concentration – mg/kg				
1–5	Control	21.9	1.7	0.07	0.6	0.4	0.2
6–10		23.2	2.4	0.03	0.3	0.3	0.2
11–19		20.0	3.2	0.29	0.4	0.4	0.2
1–5	Biosolids	26.9	1.6	0.07	0.7	0.3	0.3
6–10		31.9	1.8	0.03	0.3	0.3	0.2
11–19		26.0	3.2	0.31	0.5	0.3	0.2

Source: Dowdy et al., 1994, pp. 149–155, C.E. Clapp et al. (Eds.), *Sewage Sludge: Land Utilization and the Environment*, American Society of Agronomy, Madison, WI. With permission.

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For 20 years, biosolids were applied annually on the Rosemount, Minnesota watershed (Dowdy et al., 1994). The cumulative biosolids and trace metals applied to corn are shown in Table 5.5.The rate of application was based on the N utilization rates for continuous corn production. Corn stover and grain did not have increased concentrations of biosolids-borne Cd, Cr, Cu, Ni, or Pb during 19 years of continuous corn production.

Molybdenum is highly soluble and therefore its potential uptake by plants can be great. This is particularly true at high pH. High soil pH favors low Mo sorption and high plant availability (O'Conner et al., 2001). Because Mo toxicity occurs in cattle and other ruminants, its uptake by forage plants is important. Molybdenum toxicity has not been reported for humans (Ward, 1994). Its excess in the diet can induce Cu deficiency, resulting in a disease to ruminants known as molybdenosis. O'Conner et al. (2001) reported low Mo accumulation by corn stover, even at high biosolids' application and soil loads near 18 kg Mo ha^{-1}.

REACTIONS AND MOVEMENT IN SOILS

In the previous section of this chapter, the chemical forms of trace elements and heavy metals as related to plant uptake were discussed. Another aspect of biosolids-applied trace elements and heavy metals is their potential for movement beyond the root zone.

The nature of the chemical form of the trace element and its association with inorganic and organic soil constituents greatly affects its potential movement, retention and plant uptake (Lake et al., 1984). Soil trace elements are found in a variety of physicochemical forms (Berti and Jacobs, 1996):

- Free or complexed ions in soil solution
- Adsorbed on the surface of clays, Fe and Mn oxyhydroxides, or organic matter that are easily exchangeable
- Present in the lattice of secondary minerals such as phosphates, sulfides, or carbonates
- Occluded in amorphous materials such as Fe and Mn oxyhydroxides, Fe sulfides, or carbonates
- Present in the crystal lattices of primary minerals

To move through the soil or be taken up by plants, a metal has to be in the soil solution. Many of these physicochemical forms complex or bind the metal. There have been numerous attempts made to fractionate and identify the various forms of trace elements. Extraction with nitric acid and diethylenetrinitrilopentaacetic (DTPA) has been used to approximate total metals and plant-available metals in soils, respectively (Sposito et al., 1982; O'Conner, 1988).

An extensive review of the literature on fractionation, characterization and speciation of trace elements and heavy metals in sewage sludge and biosolids and biosolids-amended soil was conducted by Lake et al. (1984). Berti and Jacobs (1996) reported that no fractionation scheme is totally effective in dissolving each distinct form of a trace element. They indicated that the toxicity characteristic leaching

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procedure (TCLP), used to characterize leaching of heavy metals from wastes deposited in landfills, is not adequate for determining the bioavailability in soils. Baveye et al. (1999) reported that extractions using nitric acid and DTPA remove only a portion of the total metal in soils.

Dowdy and Volk (1983) reviewed the literature to identify conditions where movement and leaching of biosolids-borne heavy metals might occur. They found very little evidence of heavy metal movement beyond the zone of biosolids incorporation. Other studies (Chang et al., 1984; Williams et al., 1987) also reported that there was very little movement of heavy metals into the subsoil or below 30 cm. Dowdy et al. (1991) found that Cd and Zn concentrations were higher in the 0.32 to 0.62 m (1 to 2 ft) depth as compare to the control. Zinc concentrations increased with biosolids' application. This was not true of Cu. Relatively small amounts of biosolids-borne Cd and Zn were found in the subsoil after a 14-year period of massive biosolids' application.

CONCLUSION

Many soil and plant factors affect the bioavailability of trace elements and heavy metals to plants. Plant uptake is a function of plant species, individual trace elements, soil characteristics and sludge/biosolids characteristics. Accumulation in plants varies with the species, cultivars and organs within the plant. In general, more trace elements, including heavy metal, is concentrated in the leaves than in the fruit or grain.

A major controversy focuses on what happens to heavy metals with time. In a theory termed the "time bomb" effect, some scientists hypothesized that as organic matter decomposes, trace elements would be released into more soluble forms and result in increased uptake by plants from biosolids. Currently, long-term studies do not show that this is occurring.

Many researchers have found that the uptake of trace elements and regulated heavy metals by various crops was not linear with trace elements or sludge/biosolids' application rate; rather it approached a maximum and then leveled or decreased. This phenomenon is called the "plateau response."

Trace elements from land-applied biosolids do not appear to move through the soil profile and essentially remain in the top 30 cm. This greatly reduces the potential for heavy metal to move through the soil into ground water.

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